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The Potentiometric Effect of Hydrazine on a Belousov–Zhabotinskii Oscillating Chemical Reaction: Application to the Determination of Hydrazine

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A method for determination of hydrazine based on the Belousov–Zhabotinskii reaction is proposed. The addition of the hydrazine to the oscillating system increases the oscillating amplitude. This increase in oscillating amplitude was used as the analytical signal. To obtain a maximum value of analytical signal in determination of the hydrazine, the effects of different concentrations of malonic acid, potassium bromide, potassium bromate, cerium(IV) and sulfuric acid were investigated and the optimum concentration of each component was used for further experiments. The analytical signal is linearly proportional to the logarithm of the hydrazine concentration over the range of 1×10^{-6} M to 1×10^{-3} M (1 M = 1 mol dm^{-3}) under optimum conditions. The obtained LOD (2σ) was 1×10^{-6} M and the relative standard deviation (RSD) for five measurements of 1.1×10^{-4} M hydrazine was 5%. The influences of some potential sources of interference were also investigated.

Oscillating chemical systems are always complex and involve a large number of chemical species, which can be categorized as reactants, products or intermediates, that interact via unusual mechanisms.[1,2] During an oscillating chemical reaction, the concentrations of reactants decrease and the concentrations of intermediates or catalyst species execute oscillations (sometimes over several orders of magnitude).[2]

The best known and most widely studied oscillating chemical system is based on the Belousove–Zhabotinskii (BZ) reaction,[3] which was named after two Russian scientists who first studied the oscillatory chemical phenomenon. This reaction involves the oxidation of an organic species such as malonic acid by an acidified bromate solution in the presence of a metal ion catalyst. Among the catalysts, Ce(III)–Ce(IV) and $[Fe(II)(phen)]^{2+}$–$[Fe(III)(phen)]^{3+}$ (ferroin–ferrin) couples are two of the most widely used catalysts. In a closed (batch) system, the BZ reaction exhibits a short induction period, followed by an oscillatory phase. The color of the solution alternates between yellow and colorless (for the Ce(III)–Ce(IV) couple) with a period of approximately 1 min. The oscillations may last over 2 h. Ultimately, with concentration of the major reactants such as potassium bromate and malonic acid decreasing continuously during the reaction process, the system progresses in the direction of decreasing Gibbs free energy. In consequence, the oscillations die out and the system then drifts slowly and monotonically towards its chemical equilibrium state.

Zhabotinskii obtained a linear correlation between the reactant concentration and the period of the BZ reaction and proposed the use of this phenomenon for chemical analysis. The first paper concerning the use of regular chemical oscillations for the determination of trace amount of ruthenium(III) ion was published in 1978.[4] Since then, the advantages of the application of non-linear chemical systems under far from equilibrium condition in quantitative analysis have been reported for determinations including As^{3+},[5] Ag^{+},[6] Cl^{-},[7] Hg^{2+} and Ti^{3+},[8] $[Fe(CN)_6]^{3-}$,[3,9] ascorbic acid,[10] hydroquinone,[11] and a few others.

In practice, hydrazine is widely used in some industrial applications as catalyst, emulsifier, corrosion inhibitor, and reducing agent. It is also used as an oxygen scavenger in industry and has found wide application as an antioxidant, photographic developer, and an insecticide.[12] Hydrazine is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain glutathione,[13] so its detection has attracted considerable analytical interest.[14–18]

To our best knowledge there is no published article related to the application of chemical oscillating systems for the determination of hydrazine. In this paper, we have investigated the effect of hydrazine on the oscillating properties of "BrO_3^-–malonic acid–H_2SO_4–Ce(IV)" (BZ) oscillatory system as an matrix for determination of hydrazine.

For this purpose, the influences of different variables on the hydrazine perturbation have been optimized on the BZ oscillating system, and a logarithmic calibration curve was obtained.

Experimental

Reagents. All reagents were analytical grade (Fluka) and were used without further purification. All stock solutions of $KBrO_3$, malonic acid, KBr, H_2SO_4, and Ce(IV) salt were separately prepared in doubly distilled water. In any experiment, each reaction mixture was obtained from diluting stock solutions properly.

Apparatus. The experimental set-up used to implement the oscillating reaction consisted of a glass reaction vessel furnished with a thermostated jacket connected to a "polystat CC1" thermo-

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stat (Huber) and a magnetic stirrer (Jank & Kunkel). An "Ion-Analyzer 250" (Corning) and an "E-586 Labograph" *x–y* recorder (Metrohm) were used to record the potential changes. The electrode system included a platinum electrode as indicator and a Ag|AgCl|KCl (3 M) double junction electrode as reference electrode. To avoid the interference of chloride ion, the outer vessel of the reference electrode was filled with KNO_3 0.5 M.

Procedure. A water-jacketed glass vessel was loaded with 3 mL of each 0.35 M $KBrO_3$, 0.5 M malonic acid, 0.1 M potassium bromide, and 5.0 M H_2SO_4. After the solution had reached thermal equilibrium (25 ± 0.1 °C), the electrodes were inserted into the solution, which was stirred continuously and steadily. Then, the last species, 3.0 mL of 0.0125 M Ce(IV), was added into the system. The total volume of the reaction mixture was always 15 mL.

While adding Ce(IV) solution, the oscillations were potentiometrically recorded. When the steady state had been reached, the system was perturbed by injecting a sample including 0.1 mL of different concentration of hydrazine solution.

Based on the FKN mechanism,[19] two species are oscillating: Br^- and Ce(IV). Oscillation in Br^- concentration can be monitored using a bromide-ion selective electrode versus a reference electrode. Then, such oscillation is recorded. One of the cycles in this reaction is as follows:

$$\mathbf{Ce(IV)} \underset{-e^-}{\overset{+e^-}{\rightleftarrows}} \mathbf{Ce(III)}. \qquad (1)$$

This causes variation of the medium potential. This variation in the concentration and potential appeared as an oscillating system that can be followed with a Pt electrode using the potentiometry. On the other hand, the potential due to redox couple (Ce(IV)/Ce(III)) could be measured on the Pt electrode versus reference electrode. We have used the latter method in this research.

Results and Discussion

Effect of Variables on the Oscillation Perturbation. The effects of different variables on the oscillating reaction were studied in order to establish the optimum working conditions for the determination of species. In order to ensure the maximum sensitivity and precision of the determination, the influence of selected experimental variables in the presence and absence of an analyte were investigated using the one at a time method. For this purpose, we measured the difference in amplitude between the first oscillation after analyte injection (A) and the latest oscillation amplitude before injection (A_0) and chose this difference as an analytical signal, as follows:

$$\Delta A = A_0 - A. \qquad (2)$$

Figure 1 shows typical oscillation profiles obtained for the proposed oscillating chemical system in both the absence and presence of hydrazine perturbation under the above-described experimental conditions.

Point of Injection: However, in order to ensure accurate and high sensitive results, where the injection should be performed was a crucial variable it, therefore required careful study. During a typical oscillation cycle (Fig. 1), the potential dropped to a minimum (zone C) and then increased to the starting value (zone B), after which a new cycle was started. For the effect of hydrazine perturbation to be large, we found that the analyte should be injected in zone C, as the system began to return to the starting value.

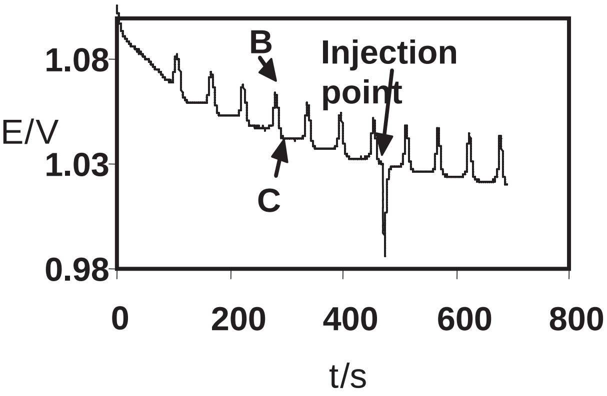

Fig. 1. Typical profile for the Ce(IV)–H_2SO_4–MA–KBr–$KBrO_3$ oscillating system with injection of hydrazine (1×10^{-4} M). The solution condition; 0.11 M $KBrO_3$, 0.1 M MA, 1.0 M H_2SO_4, 2.6×10^{-3} M Ce(IV), and 0.02 M KBr. The temperature was 25 ± 0.1 °C.

KBr: Based on the FKN mechanism,[19] Br^- is an intermediate that plays an important role in a feedback mechanism and oscillation; it appears and disappears during the reaction. It is not necessary to add Br^- as a reactant to start the reaction, but to do so decreases the period induction and thus the experiment duration. As can be seen in Fig. 2a, the effect of Br^- concentration on the analyte perturbation was studied over the range of 0.002 to 0.020 M. According to obtained results, 0.02 M Br^- concentration was chosen as optimum.

Malonic Acid: The effect of the malonic acid was studied over the range from 0.10 to 0.50 M. The oscillation amplitude decreased but the frequency increased for increasing malonic acid concentration. As can be seen from Fig. 2b there was an optimum concentration (0.10 M), at which the system responded better to the analyte perturbation.

Ce(IV): The BZ reaction is catalyzed by a metal ion. In this work, Ce(IV) catalyzed the BZ reaction. Then, the Ce(IV) concentration should be optimized. It was investigated in the range of 0.0015 to 0.01 M concentrations and 0.0025 M was chosen as the optimum (Fig. 2c).

H_2SO_4: Based on the overall BZ reaction and the FKN mechanism, the reaction takes place in a strongly acidic medium.[19] Therefore, the oscillating properties and sensitivity were investigated in the range of 1.0 to 2.5 M H_2SO_4 concentration (Fig. 2d); consequently, 1.0 M of H_2SO_4 was chosen as the optimum concentration.

$KBrO_3$: Increasing of $KBrO_3$ concentration from 0.05 to 0.20 M caused the amplitude and the frequency of the oscillations to increase. Variation of $KBrO_3$ concentration strongly affected the analyte perturbation (Fig. 2e). In 0.07 M concentration, the sensitivity was maximum.

Determination of Hydrazine. The oscillating system was perturbed with various concentrations of hydrazine under the above-described optimum conditions. When hydrazine was added to the system the oscillation amplitude increased. A typical oscillation carried out in the above optimum experimental condition in the presence of increasing concentrations of hydrazine is plotted in Fig. 3a. Several repeated experiments in-

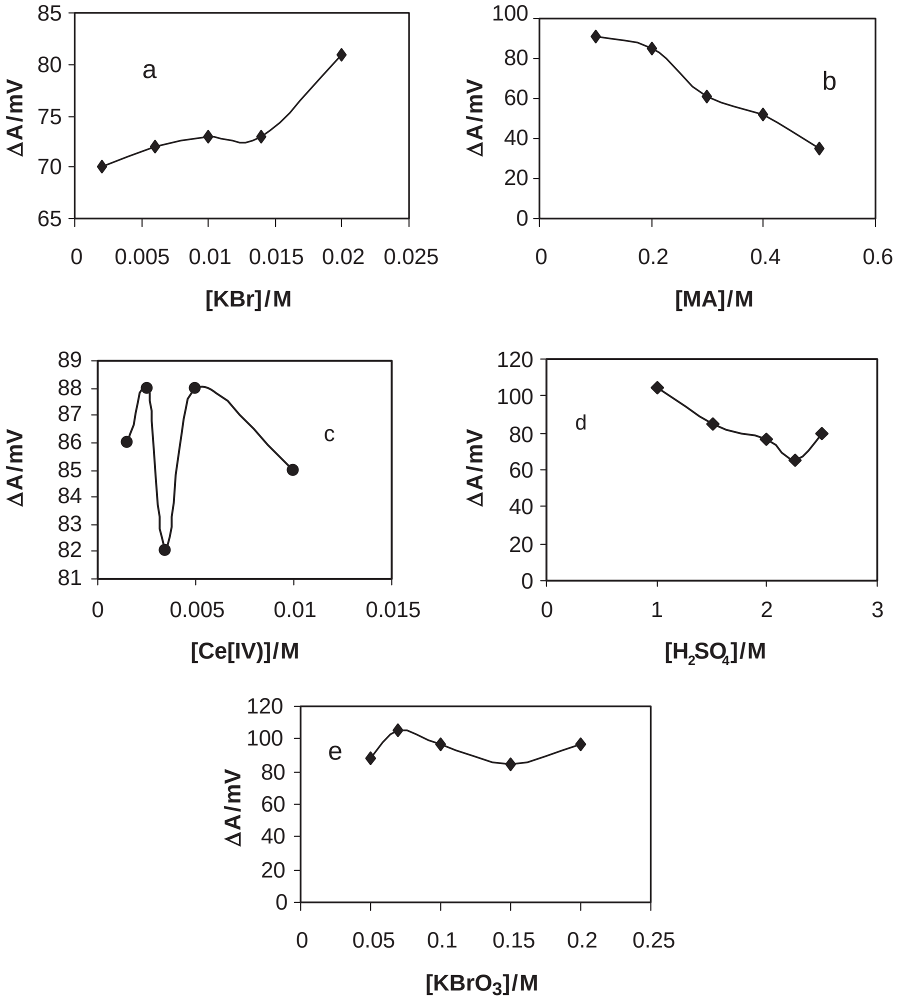

Fig. 2. Effect of concentration of (a) potassium bromide, (b) malonic acid, (c) Ce(IV), (d) sulfuric acid, and (e) potassium bromate on the perturbation of hydrazine on the BZ oscillating chemical reaction. (a) 0.2 M $KBrO_3$ + 1.5 M H_2SO_4 + 0.001 M Ce(IV) + 0.35 MA; (b) 0.2 M $KBrO_3$ + 1.5 M H_2SO_4 + 0.001 M Ce(IV) + 0.02 M KBr; (c) 0.02 M KBr + 1.5 M H_2SO_4 + 0.5 M MA + 0.2 M $KBrO_3$; (d) 0.20 M $KBrO_3$ + 0.10 M MA + 0.0025 M Ce(IV) + 0.02 M KBr, and (e) 0.20 M KBr + 0.10 M MA + 1.0 M H_2SO_4 + 0.025 M Ce(IV). In all cases, the concentration of injected hydrazine was 1×10^{-4} M.

Table 1. The Figure of Merits of Some Methods Developed for Determination of Hydrazine

Method	Linear dynamic range	LOD	Ref.
Differential pulse voltammetry	0.3–500 $\mu g\,L^{-1}$	0.1 $\mu g\,L^{-1}$	14
Kinetic-spectrophotometric	3.0×10^{-5}–3.2×10^{-5} M	8.5×10^{-8} M	15
Chromatography with amperometric detection	0.001–0.06 ppm	0.4 ppb	16
Modified carbon paste electrode	5–60 $\mu mol\,L^{-1}$	1.0 $\mu mol\,L^{-1}$	17
Flow injection chemiluminescence	5.0×10^{-7}–1.0×10^{-4} M	2.0×10^{-7} M	18
Oscillating chemical reaction	1×10^{-6} to 1×10^{-3} M	1×10^{-6} M	This work

dicated that there is a good linear relationship between the changes in the oscillation amplitude (ΔA) and the logarithm of hydrazine concentration, in the range of 1×10^{-6} M to 1×10^{-3} M (Fig. 3b). If the concentration of hydrazine exceeds 1.0×10^{-3} M, the oscillation amplitude increasing does not have a linear relationship with logarithmic concentration.

The calibration data obey the following logarithmic regression equation with a correlation coefficient of 0.99:

$$\Delta A = 49.81 \log[\text{hydrazine}] + 298.03. \tag{3}$$

The detection limit was obtained to be 1×10^{-6} M. The relative standard deviation for the determination of hydrazine concentration at 1×10^{-4} M was obtained to be 4% for 5 measurements. Table 1 shows our work versus other hydrazine determinations.

Interferences. Oscillating systems are very easily altered by the presence of foreign species or ions in the reaction medium. Consequently we investigated the effect of some potential sources of interference in the above-described optimum condition. According to Table 2, large amounts of some cat-

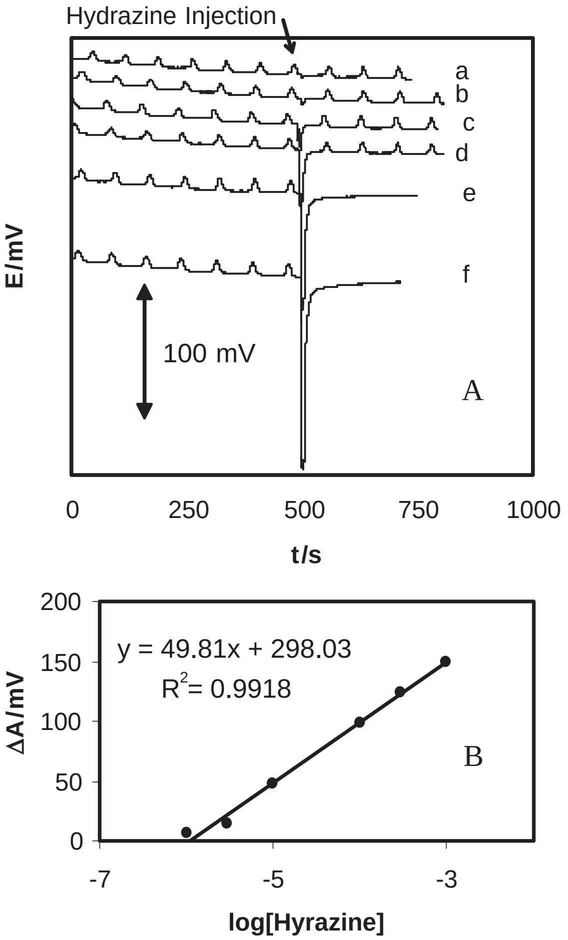

Fig. 3. A) Typical oscillation profiles of BZ system in the presence of increasing concentrations of hydrazine; a) 1 μM, b) 3 μM, c) 10 μM, d) 100 μM, e) 300 μM, and 1000 μM. B) Dependence of the increase in the oscillating amplitude versus hydrazine concentration. Solution condition was 0.0025 M Ce(IV), 0.10 M MA, 0.020 M KBr, 0.07 M $KBrO_3$, and 1.0 M H_2SO_4. The temperature was 25 ± 0.1 °C.

Table 2. Influence of Foreign Ions and Species on the Determination of Hydrazine

Ions	Tolerated ratio
La^{3+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, NO_3^-, $H_2PO_4^-$	2000
Ca^{2+}, K^+, Na^+, Mg^{2+}, HPO_4^{2-}, Zn^{2+}, Mn^{2+}, Cd^{2+}	1000
Cl^-, I^-, Hg^{2+}	10

ions and anions such as alkali and alkaline earth ions have no effect, but ions such as I^-, Cl^-, and Hg^{2+} have moderate effects on the determination of hydrazine.

Conclusion

As described above, kinetic methods of analysis, especially chemical oscillating reactions are currently regarded as being highly effective tools in analytical chemistry. Thus, we attempted to determine the hydrazine using its perturbation effect on the classic BZ reaction.

The injection of the hydrazine solution changed the oscillating amplitude. This change had a logarithmic relationship with hydrazine concentration over the range of 1×10^{-6} M to 1×10^{-3} M with an equation of "$\Delta A = 49.81 \log$ [hydrazine] $+ 298.03$" and a regression coefficient of 0.99.

Comparison of the results with other methods (Table 1) shows that, although, this method does not have ideal analytical attributes (e.g., detection limit, %RSD, ...), still the results are acceptable and comparable with other results. In other words, the largest advantage is its simplicity in technique and instrumental set-up.

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